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SUMMARY

Mercury cadmium telluride (HgCdTe) offers attractive possibilities for fast, elevated-operating-temperature infrared detection from 1- to 20-micro-meter (μm) wavelengths, particularly in the 8- to 14-μm wavelength region for which it was developed. HgCdTe is considered for use in satellites for terrestrial, atmospheric, and ocean mapping; infrared astronomy; and optical communications. Its chemical stability in the space environment is open to some question; however, experimental data so far accumulated at NASA-ERC indicate that it is marginally adequate for such purposes. Some attention is given to the possibility of operation using (passive) space radiative cooling; this would eliminate the need for cryogens and provide a much longer operating lifetime as well as reductions in size and weight of the detector system.

INTRODUCTION

HgCdTe is an alloy of the two II-VI semiconductor compounds, mercury telluride (HgTe) and cadmium telluride (CdTe), which have tellurium as a common element. HgTe has a forbidden energy gap near zero, while that of CdTe is about 1.5 eV in the operating temperature range of interest. The forbidden energy gap of the alloy HgCdTe is a function of the relative proportions of HgTe and CdTe, and its range lies between these extreme values. For a long wavelength cutoff of 14 microns (beyond which the detector is insensitive), the desired forbidden energy gap of the alloy is 0.09 eV. This represents an HgCdTe composition of approximately 85 mol % mercury telluride and 15 mol % cadmium telluride.

THEORETICAL STABILITY CALCULATION

Cadmium telluride (CdTe) is the more stable of the two compounds and will be considered first. The direct decomposition may be represented by the chemical equation

$$CdTe \ (s) \longrightarrow Cd \ (g) + 1/2 \ Te_2 \ (g),$$
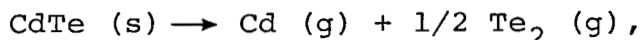
where s and g, respectively, refer to the solid and gaseous states. In customary vacuum dewar storage of the detector, the elemental Cd and Te resulting from surface decomposition would be evolved and thus the reaction would be essentially irreversible as shown. At constant (operating) temperature, the following thermodynamic relation is useful:

$$\Delta F = \Delta H - T\Delta S = -RT \ln K$$

where ΔF, ΔH, and ΔS, respectively, are the free energy, enthalpy, and entropy changes occurring during the reaction, T is the absolute temperature, R is the gas constant in consistent units, and K is the equilibrium constant for the reaction indicating the extent of the decomposition:

$$K = P_{Cd} \; P_{Te_2}^{1/2}$$

where P indicates the partial pressures of the subscript elements. This equilibrium constant is not a function of pressure, but reduced pressure storage changes the material activities so that the system volume will increase. For solids, the effect is generally negligible.

The effect of temperature on the equilibrium constant K is given by

$$\frac{d(\Delta F/T)}{dT} = \frac{-\Delta H}{T^2}$$

where

$$\Delta H = \int_{T_1}^{T_2} C_p \, dT \; .$$

T_1 and T_2 are the initial and final temperatures and Cp is the heat capacity of the material at constant (storage) pressure.

Since the reaction for the formation of the compound is exothermic (involves heat), the decomposition equilibrium constant will increase with temperature. The data in Table I are available for enthalpy and entropy changes in CdTe. The entropy

TABLE I - HEATS AND ENTROPIES OF FORMATION FOR CdTe

Reference	ΔH_F^*,kcal/g.mol at 25°C	ΔS_F,cal/g.mol(°K) at 25°C	ΔH_D^*,kcal/g.mol at 25°C	600°C	ΔS_D,cal/g.mol (°K) at 600°C
1	24.0	23.0	140.7	134.0	86.4
4	22.3	26.6			
5	24.3	22.6			
6	24.8	20.			

$$C_p \text{ (CdTe)}^7 = 11.79 + 2.06 \times 10^{-3} T \text{ cal/g.mol(°K)};$$

$$C_p \text{ (Cd)}^8 = 5.46 + 2.47 \times 10^{-3} T; \text{ and}$$

$$C_p \text{ (Te)}^8 = 5.19 + 2.50 \times 10^{-3} T.$$

* Subscripts F and D, respectively, represent formation from the elements and decomposition to the elements, according to the reaction.

$$2 \text{ CdTe(s)} \rightleftharpoons 2\text{Cd(g)} + \text{Te}_2\text{(g)}.$$
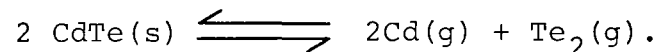
change may be calculated from

$$\Delta S = \int \frac{dQ \text{ rev.}}{T} = \int \frac{C_p \, dT}{T} = \int (\Delta a + T\Delta b) \frac{dT}{T}$$

evaluated between the temperature limits desired. Using the data of reference 1 gives:

$$\Delta S_D (298^O K) = 86.4 + \int_{873}^{298} [(5.46 + 5.19 - 11.79)$$

$$+ (0.00247 + 0.00250 - 0.00206) T] \frac{dT}{T}$$

$$= 86.0 \text{ cal/g.mol } (K^O)$$

and

$$\Delta F_D (298^O K) = \Delta H_D - 298 \Delta S_D$$

$$= 140,700 - 298 (86.0)$$

$$= 114,900$$

$$= -RT \ln K .$$

The decomposition equilibrium constant may now be calculated:

$$K = \exp(-\Delta F_D / 2RT)$$

$$= \exp[-114,900/1.99 (298)(2)]$$

$$= 10^{-42}$$

Thus, at room temperature ($25^{\circ}C = 298^{\circ}K = 77^{\circ}F$),

$$P_{Cd}P_{Te_2}^{1/2} = 10^{-42} \text{ (vanishingly small)}.$$

For mercury telluride, comprising about 85 mol % of the detector, the data in Table II are available for the decomposition reaction involving solid elemental tellurium (ref. 1).

TABLE II - HEATS AND ENTROPIES FOR HgTe DECOMPOSITION

ΔH_D, kcal/g.mol* at $493^{\circ}K$	ΔS_D, cal/g.mol$(^{\circ}K)$* at $493^{\circ}K$	C_p, cal/g.mol$(^{\circ}K)$*
26.8	31.2	$10.65 + 5.9 \times 10^{-3}T$

*Ref. 1.

Proceeding in the same fashion as for CdTe, one obtains:

$$\Delta F_D \ (493^{\circ}K) = \Delta H - T\Delta S$$

$$= 26,800 - 493 \ (31.2)$$

$$= 11.400 \text{ cal/g.mol,}$$

and

$$K = \exp[-11,400/1.99 \ (493)]$$

$$= 9.33 \times 10^{-6}$$

$$= P_{Hg} \ ,$$

comparing favorably with experimentally determined values using the Knudsen method (ref. 1).

In summary, the equilibrium decomposition pressure of tellurium above mercury cadmium telluride infrared detectors is very small up to the semiconductor alloy melting point (which is a function of alloy composition, but roughly 700°C for compositions of interest). Pure CdTe melts at 1045°C, while pure HgTe decomposes below 600°C.

The decomposition pressure of mercury above mercury cadmium telluride is orders of magnitude higher, while that of cadmium is intermediate. Selected data are given in Table III.

TABLE III - DECOMPOSITION PRESSURES OF ELEMENTS OVER HgCdTe

T, °K	T, °C	P_{Hg}, torr	P_{Cd}, torr	PTe_2, torr
298	25	3.0×10^{-10}	*Negligible	*Negligible
373	100	1.3×10^{-6}	5.0×10^{-13}	*Negligible
473	200	1.9×10^{-3}	8.0×10^{-9}	1.5×10^{-12}
673	400	4.0	3.1×10^{-4}	3.0×10^{-6}
873	600	550	0.15	7.8×10^{-3}

*Negligible is defined here as below pressures found in deep space (arbitrarily, those below 10^{-14} torr). Interpolation between tabular figures may be made since log P vs $(10^3/T°K)$ is a straight line for HgTe and CdTe (ref. 1).

Data on absolute pressures in deep space have been published (ref. 2). A brief summary is given in Table IV.

Obviously, the decomposition reaction is largely irreversible if the absolute storage pressure of the semiconductor detector is maintained lower than the decomposition partial pressures of the elements. Intrinsic infrared detectors are very thin and of relatively large surface area; hence, gaseous elements evolved would dissipate into the surrounding space. The evacuated dewar volume in all cases is much greater than that of the detector, and thus represents a nearly infinite sink for decomposition products; in addition, small leaks to the outside of the satellite in deep space would tend to decrease the absolute pressure in the dewar vessel still further.

TABLE IV – AMBIENT SPACE PRESSURES AT VARIOUS ALTITUDES

Altitude, kilometers (Distance from Earth)	Average pressure, torr
200	3×10^{-7}
500	3×10^{-9}
10^3	10^{-11}
10^4	3×10^{-14}
10^5	Approx. 3×10^{-15}

Thus the data indicate that the detector should not be subjected for any appreciable period of time to temperature higher than those indicated in Table V for the given dewar storage pressures. A pressure of 10^{-6} torr would represent a typical initial evacuated dewar pressure, and the higher vacua potential pressures if the dewar slowly leaked to deep space. Mercury telluride decomposition is the limiting stability factor in all cases.

TABLE V – LIMITING PRESSURE-TEMPERATURE STORAGE RELATIONSHIPS FOR HgCdTe

Storage pressure, torr	Maximum permissable Detector Temperature to avoid decomposition		
	°K	°C	°F
10^{-6}	370	97	207
10^{-8}	326	53	127
10^{-10}	291	18	64
10^{-12}	260	-13	9
10^{-14}	235	-38	-36

BACKGROUND LIMITED OPERATING TEMPERATURE

An analysis of expected background-limited infrared photoconductor (BLIP) temperatures for HgCdTe follows. With spherical energy bands assumed and a state for each of the two carrier spins, the following equations may be written for the concentration of carrier states N and for electrons n and holes p (ref. 3):

$$dN = \frac{4\pi}{h^3}(2m*)^{3/2} E^{1/2} dE = N(E) dE$$

$$n = f(E)N(E) = 2\left(\frac{m_e^* kT}{h^2}\right)^{3/2} E^{(E_f - E_c)kT}$$

$$p = 2\left(\frac{m_h kT}{h^2}\right)^{3/2} E^{(E_v - E_f)/kT}$$

Thus,

n_t = thermally-generated carrier concentration

$$= 2\left(\frac{2\pi kT}{h^2}\right)^{3/2} (m_e^* m_h^*)^{3/4} E^{-E_g/2kT}$$

and

N_B = background-generated carrier concentration

$$= \frac{F\eta\tau}{t} \int_0^{co} Q(\lambda, 300^\circ K) \, d\lambda$$

where

λ_{co} = cutoff wavelength

$$= \frac{hc}{E_G} = \frac{1.24}{E_{G, eV}} \text{ microns.}$$

If one assumes a 1-μsec lifetime independent of temperature in this region, one gets the following results:

λ_{co}, microns	BLIP Temperature ^{O}K
14	78
9	100
7	112

Experimentally, for a detector of this material having peak spectral response at 10 to 13 μ (λ_{co} = 14 μ), it has been found that the BLIP temperature ($300^{O}K$ background, $60^{O}FOV$) is roughly that of boiling nitrogen ($77.3^{O}K$). Thus, these calculated results appear approximately correct. All of these BLIP temperatures will be lower as the background temperature is reduced. Thus, performance less than background-limited performance is indicated at temperatures above $100^{O}K$.

Most of the work reported here has been performed on photoconductive (PC) detectors. It is not yet possible to create p-n junctions at will in this material; hence, only a few PV detectors have been tested. PEM detectors are not popular for space applications because of the relatively heavy magnet.

Photon-noise-limited performance is indicated if fluctuations in arrival rate of photons from the background are smaller than the arrival rate of target photons (within the spectral range of the detector).

λ_{co}, microns	Photon-noise-limited temperature, ^{O}K
14.5	83
4	93

Thus, photon noise temperature is only a weak function of E_G (composition) in HgCdTe. Photon-noise-limited performance may be accomplished in two steps (ref. 9):

1. Reduce thermal noise below G-R noise:

$$\frac{V_N(T)}{V_N(G-R)} \qquad \frac{nA(\mu q\ kT)^{1/2}}{I(\tau)^{1/2}} < 1$$

This may be done by

(a) Lowering the operating temperature T,
(b) Reducing the carrier concentration n,
(c) Lowering the carrier mobility μ,
(d) Reducing device cross-sectional area,
(e) Imposing a high bias current I.

2. Reduce G-R noise below photon noise:

(a) Reduce lattice temperature (not available),
(b) Increase lifetime (τ) associated with lattice
     carrier generation until longer than that
     associated with photon generation. This in-
     volves higher crystal lattice perfection (lower
     impurity and other defect concentrations).

These, then are methods by which performance in this material
may be improved at elevated operating temperature.

EXPERIMENTAL STABILITY DATA

A wafer of bulk mercury cadmium telluride material and an
HgCdTe detector were subjected to various temperature-pressure
combinations to determine the extent of chemical decomposition
under various conditions. Residence time for each P-T combina-
tion was 1 hour. Temperatures up to 550°C and absolute pressures
down to 2×10^{-7} torr were investigated. Weight losses in the bulk
material (primarily caused by HgTe decomposition) and performance
degradation in the detector were used as decomposition criteria.

The weight loss data have been calculated and expressed as
percent losses based on the original (before treatment) sample
weights. The radiant source used for testing the HgCdTe detec-
tor was a uniformly heated filament in a cavity; the performance
data are recorded as $\Delta R/R_d$, where ΔR represents the difference
between light and dark detector resistances, and R_d the dark
resistance.

The data are presented in Table VI.

DISCUSSION

It is reasonably evident that storage of HgCdTe detectors
in an evacuated dewar at ambient (or lower) temperatures will
cause little decomposition of the material. Since the operating
temperature of these detectors is approximately the normal
boiling point of nitrogen (77.3°K or -195.8°C), these detectors
may also be safely stored at operating temperatures.

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TABLE VI - PERFORMANCE DATA

Temperature $^\circ C$	Pressure, torr (mm Hg)	% Weight Loss = $(100\ \Delta W)/W$	$\Delta R/R_d$
25	760	0	0.851
25	10^{-6}	0	0.851
100	10^{-6}	0.0229	0.680
200	10^{-3}	0.0630	0.630
200	10^{-4}	0.110	0.798
200	10^{-6}	0	0.812
400	10^{-3}	0	0.824
400	10^{-4}	0.0366	0.824
400	10^{-6}	0	0.822
550	10^{-3}	0.457	0 (open)
550	10^{-4}	0.110	0
550	10^{-6}	0.128	0
550	2×10^{-7} (system ultimate)	0.0918	0

During satellite operation in the hard vacuum of space, if the dewar leaks, the HgCdTe device will be exposed to appreciably lower pressures than those obtainable in this investigation using the NRC vacuum system shown on the following page. At operating temperature, decomposition (from free energy calculations presented earlier in this work) is probably negligible. Thus, no pressurized chamber is required. Indeed, this would require a separate and larger infrared transmitting window for the chamber, and would require selection of dry special gases to prevent frosting or other condensation on refrigerated dewar internal areas. At ambient temperature ($25^\circ C$), absolute pressures have to fall to 3×10^{-10} torr before appreciable HgTe decomposition will occur.
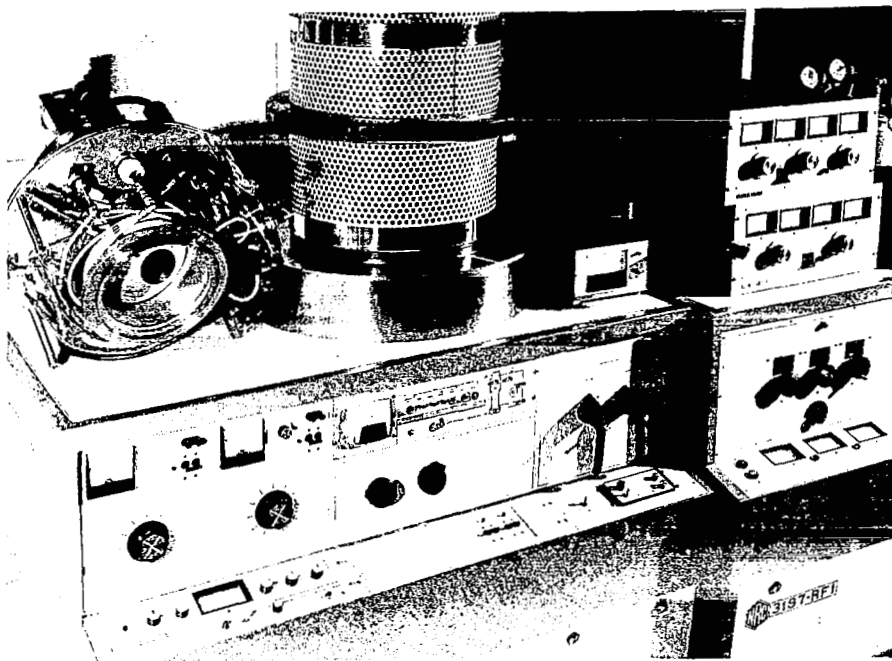
Vacuum System Used for Experimental Investigation

At higher temperatures (and pressures not lower than 10^{-6} torr), the device continues to give good response through 400°C. Above this temperature, decomposition sets in as shown by both the weight loss and detector performance data.

It is difficult to compare actual with predicted (theoretical) decomposition because the experimental partial pressures of decomposition products depend on the ratio of system to semiconductor volume and the total system pressure. However, the following sample calculation suffices to show that theory and experiment are not inconsistent.

At 200°C and 10^{-3} torr pressure, consider the decomposition of a 10-μm IR detector (forbidden bandgap $E_g = 0.1$ eV, $\lambda_{co} = 12.4$ μm, and composition approximately 88 mol % HgTe, 12 mol % CdTe). Typical dimensions would be 3 mm×1 mm (1 mm square sensitive area) and 25 μm thick, for a total volume of 0.075 mm^3. The dewar vacuum space will by typically 10 cm^3, for a volume ratio of $10/0.075 \times 10^{-3} = 1.33 \times 10^5$. The decomposition pressure of mercury over HgTe at 200°C is 1.9×10^{-3} torr (those of Cd and Te are negligibly small, respectively, 8×10^{-9} and 1.5×10^{-12} torr). The HgCdTe detector will decompose until the (mercury) decomposition pressure equals the existing system pressure; then there will be no further decomposition in a closed system because of the lack of a driving force.

HgCdTe specific gravity (determined on bulk ingot, melt grown, both by measurement and liquid displacement) = 7.44 g/cm^3.

Weight of typical HgCdTe detector = 0.0.075(10^{-3})(7.44) = 5.59×10^{-4} grams.

$$\frac{\text{Gram atoms}}{\text{Hg available}} = \frac{5.59\times10^{-4}(0.88)(200.61)}{0.88(328.22) + 0.12(240.02)}$$

$$= 1.55\times10^{-6}$$

On the assumption of an ideal gas (an excellent assumption at this very low pressure), this much mercury (total decomposition) could occupy 1.55×10^{-6}(22.4)(760/1.9×10^{-3})(473/273) = 24 liters at 1.9×10^{-3} torr and 200°C.

This means that in a 10cm^3 free volume dewar decomposition would be only (10/24,000)(100) = 0.0714% complete before the mercury pressure rose to its (dynamic) equilibrium value and further net decomposition ceased. The extremely small equilibrium partial pressures of cadmium and tellurium are negligible but would tend to further inhibit decomposition.

CONCLUSIONS

Mercury cadmium telluride infrared detectors deteriorate rapidly, even in storage, at temperatures above 500°C and moderate (or higher) vacua. Under no circumstances should they be exposed to these temperatures. Thus, glass or metal dewars containing HgCdTe should not be "baked out" during any evacuation.

Decomposition (as evidenced by weight loss) begins to be measurable at temperatures above ambient (25°C). Although device deterioration was not observed during the present investigation at 400°C and less, repeated evacuation of the space surrounding the detector would cause successive decompositions (mercury losses) and eventually would alter the chemical identity of the semiconductor sufficiently so that the detector could not function.

The normal operating temperature of HgCdTe detectors is 77°K, the atmospheric pressure boiling point of nitrogen. It would be desirable to store and keep detectors at or near operating temperature during their useful life if this can be done.

As shown in the section on background limited operating temperature, HgCdTe detectors work well at the normal boiling

point of nitrogen (77.3^{O}K), and hence offer a big advantage over the traditional mercury-doped germanium (operating temperature 30°K or lower) for the 8- to 14-μm wavelength atmospheric window spectral region. Two other important features of HgCdTe detectors are a much higher optical absorption coefficient (greater quantum efficiency) and a much lower device resistance.

REFERENCES

1. Goldfinger, P. and Jeunehomme, M.: Mass Spectrometric and Knudsen-Cell Vaporization Studies of Group 2B-6B Compounds. Faraday Soc., Vol. 59, 1963, pp. 2851-2866.

2. Santeler, D. J., Holkeboer, D. H., Jones, D. W., and Pagano, F.: Vacuum Technology and Space Simulation. NASA SP-105, 1966, pp. 5, 34.

3. Hannay, N. B.: Semiconductors. Reinhold Publishing Co., New York, 1951, pp.14-29.

4. Korneeva, I. V., Belyaev, A. V., and Novoselova, A. V.: Vapor Pressure of Solid Tellurides of Zn and Cd. Zhnurnal Neorganicheskoi Khimii, Vol. 5, 1960, pp. 3-7.

5. Kelley, J.: United States Bureau of Mines Bulletin No. 592, 1961, pp. 5-32.

6. Lorenz, M. R.: The Solid-Vapor Equilibrium of CdTe. Physics and Chemistry of Solids. Vol. 23, 1962, pp. 1449-1451.

7. Drowart, J., and Goldfinger, P.: A Thermodynamic Study of III-V and II-VI Compounds by Mass Spectroscopy. Chimie Physique, Vol. 55, 1958, pp. 721-732.

8. Perry, J. H.: Chemical Engineers' Handbook, Third Edition. McGraw-Hill Book Company, New York, 1950, pp. 219-232.

9. Kruse, P. W., McGlauchlin, L. D., and McQuistan, R. B.: Elements of Infrared Technology. John Wiley and Sons, New York, 1962, pp. 377-382.